Supporting information for

Rapid and selective removal of toxic and radioactive anionic pollutants using an ionic covalent organic framework (iCOF-2)

Atikur Hassan,† Md Mofizur Rahman Mollah,§ Soumen Das,§ Neeladri Das*†

†Department of Chemistry, Indian Institute of Technology Patna, Patna 801106, Bihar, India

§ Materials Chemistry and Metal Fuel Cycle Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, Tamil Nadu, India

Corresponding Author. E-mail: [neeladri@iitp.ac.in,](mailto:neeladri@iitp.ac.in) neeladri2002@yahoo.co.in

Tel.: +91 9631624708

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Raw Materials: Resorcinol, guanidinium chloride and hydrazine hydrate were procured from Merck. All the other reagents and solvents were purchased locally and were used as obtained without further purification. Distilled water was used for all the capture experiments, unless otherwise specified. Water samples from various sources(such as tannery, pond, lake and river) were collected from industrial and rural areas of Kolkata, India. A sample of sea-water was collected from Chennai (Marina beach), India.

Characterization:

Fourier transform infrared spectra (FTIR) of samples were collected using the ATR mode of a PerkinElmer 400 FT-IR spectrophotometer. Solid-state ¹³C CP-MAS NMR spectrum of iCOF-2 was recorded with 400 MHz Bruker NMR instrument. Solution phase NMR were also recorded on 400 MHz Bruker NMR. Powder X-ray diffraction (P-XRD) patterns were obtained using a GNR XRD with Cu Kα radiation ($\alpha = 1.5406$ Å) at a scan rate of 2°/min. Thermogravimetric analysis (TGA) of iCOF-2 samples were performed by using a SDT Q600 (TA Instruments) equipment. The experiments were carried out in the temperature range of 30−700 °C, under nitrogen atmosphere with regulated heating rate of 10°C/min. The porous nature of the material and its surface area were determined using Quantachrome Autosorb iQ₂ instrument (Quantachrome, USA). Prior to analysis, a given sample was activated at 120 °C for 12h. Following activation, the sample was subjected to gas adsorption measurements ($P/P₀$) range from 0 to 1 atm.) at 77 K. The Brunauer-Emmett-Teller (BET) model was employed for the calculation of the specific surface area of iCOF-2. The distribution of pore size was obtained from the nitrogen gas sorption curves utilizing the non-local density functional theory (NL-DFT). Zeta-potential data was obtained using Anton Paar Lite sizer 500 with 100 runs (manual mode). Morphological studies were done using a ZEISS Field Emission Scanning Electron Microscope (FE-SEM). Before analysis, the samples were sputter-coated with gold. A voltage of 20 kV was applied to perform elemental analyses and mapping with energy dispersive elemental analysis technique (EDX). Atomic Force Microscope (AFM) images were taken using an Agilent instrument. Irradiation experiments for iCOF-2 samples were performed at various dose levels such as 50 kGy, 100 kGy, 200 kGy and 300 kGy for 3.2 days, 6.4 days, 12.8 days and 19.2 days respectively. UV-visible absorption spectra were recorded on a Shimadzu UV-2550 UV-vis spectrophotometer. Raman spectra were obtained using a laser of 532 nm on a Renishaw Ramanscope system (micro-Raman spectrometer). All the images reported herein were captured using Canon DSLR or Motorola moto g60 mobile camera.

Synthesis of triformylresorcinol (TFR)¹ -

A mixture of resorcinol (1g, 9.1 mmol) and hexamine (HMTA: hexamethylenetetramine) (2.79 g, 19.9 mmol) were dissolved in 15 mL trifluoroacetic acid (TFA) under an argon atmosphere. The reaction mixture was refluxed at 120 °C for 24 h, and then heated at 150 °C for additional 3h. Subsequently, the reaction mixture was cooled to 100 °C and treated with 20 mL 3M HCl. After the addition of HCl, the formation of a yellow precipitate was observed within 5 minutes. Reaction mixture was heated for additional 30 minutes at 120 °C. The crude products thus obtained were filtered and washed repeatedly with ethanol until the filtrate was clear. The desired product was obtained as a powder after drying in oven at 60 °C for several hours.

Fig. S1: ¹H NMR of the TFR

Synthesis of triaminoguanidium chloride (TAG_{Cl})²-

To a mixture of 1.91 g (20 mmol) guanidine hydrochloride and 3.41 g (106 mmol) hydrazine hydrate, 10 ml of 1,4-dioxane was added while stirring continuously. The mixture was refluxed for 2 hours. The reaction mixture was then allowed to cool to room temperature and the product was filtered. The product was then washed with 1,4-dioxane and dried to give triaminoguanidinium chloride (TAG_{Cl}) .

Synthesis of iCOF-2

1,3,5-triformylrecorcinol benzene (42 mg, 0.2 mmol) and triaminoguanidinium chloride (28 mg, 0.2 mmol) were dissolved in solvent containing 2:0.6 v/v ratio of 1,4 Dioxane and water with continuous stirring. Later, the reaction mixture was charged into a Pyrex tube and sonicated for 10 min. The reaction mixture was maintained at 120 °C for 3 days and later cooled to room temperature. iCOF-2 was obtained as dark yellow precipitate (57 mg).

Synthesis of Sa-TAGCl monomer ² (model compound)

Triaminoguanidinium chloride (2.34 g, 0.017 mol) was dissolved in a hot mixture of ethanol (54 mL) and water (27 mL). A solution of 2- hydroxybenzaldehyde (0.05 mol) in ethanol was slowly added to it. The resulting mixture was refluxed and the precipitate of Sa-TAG_{Cl} model compound [N',N'',-2-tris((E)-2-hydroxybenzylidene)hydrazine1-carbohydrazonhydrazide hydrochloride] was collected accordingly. The precipitate was washed with acetone and dried under reduced pressure. The obtained product (Sa-TAG_{Cl}) was characterized using FT-IR and NMR spectroscopy.

Fig. S4: ${}^{13}C({}^{1}H)$ NMR of Sa-TAG_{Cl}

Fig. S5: FTIR spectrum of Sa-TAG_{Cl}

 Fig. S6: P-XRD of monomers

Fig. S7: Zeta potential analysis of iCOF-2

Fig. S8: TGA thermogram of iCOF-2

Name of the compounds	BET Surface area	References						
	(m^2/g)							
iCOF-2	306.86	This work						
CON-Cl	220	J. Am. Chem. Soc. 2018, 140, 896-899						
		J. Am. Chem. Soc. 2016, 138, 2823-2828						
$TpTG_{Cl}$	267							
DATG _{CI} -iCONs	155	ACS Appl. Mater. Interfaces 2020, 12, 13248-13255						
TGH+•PD	16	Nat Commun. 2022, 13, 3904						
$BT-DGCl$	$\overline{3}$	Environ. Sci. Technol. 2019, 53, 878-883						
$ICOP-1$	198	ACS Sustainable Chem. Eng. 2019, 7, 1564-1573						
POF1	200	Chem. Sci., 2020,11,7910-7920						
$TFPB-TGCl-iCOF$	228	J. Mater. Chem. A, 2020, 8, 12657-12664						
TFPT-TG _{CI} -iCOF	454							
TG-DFP	53	Chem. Mater. 2019, 31, 4148-4155						
IPOF-Cl	163	Nanoscale, 2021,13,3967-3973						
BdaTG _{Cl}	66.3	Chem. Eng. J, 2022, 428131124						
DhaTG _{Cl}	96	Environ. Sci. Technol. 2019, 53, 5212-5220						
$iCON - I$	12.50	ACS Appl. Nano Mater. 2021, 4, 12, 13319-13328						
COFTGTp	152.8	J. Hazard. Mater., 2022 435 128965						

Table -S1: Comparison of BET surface area: (iCOF-2 vs literature reported iCOFs /iCONs)

Fig. S9: BET plot of iCOF-2

Fig. S10: Pore size distribution of iCOF-2

Fig. S11: AFM micrographs of iCOF-2

Element	Weight%	Atomic%
CK	53.71	59.41
NK	26.39	25.03
OK	17.79	14.77
CIK	2.12	0.79
Totals	100.00	

c q $¹$ </sup> 0 0.5 1 1.5
Full Scale 54232 cts Cursor: 0.000 $\frac{1}{2}$ 2.5 $\overline{\mathbf{3}}$ 3.5 4

Fig. S12: EDAX analysis of iCOF -2

Fig. S13: FE-SEM image of NaOH treated iCOF-2

Fig. S14: P-XRD plots of pristine iCOF and acid/base treated iCOF-2

Fig. S15: TGA thermograms of pristine iCOF-2 and acid/base treated iCOF-2

Fig. S16: FT- IR spectra of pristine iCOF and acid/base treated iCOF-2

Methods:

Capture studies: iCOF-2 was used to capture various anionic pollutants from respective aqueous solution. Solutions of varying concentration of MnO_4^- , ReO_4^- , I_3^- , CrO_4^{2-} , $Cr_2O_7^{2-}$, and diclofenac were prepared for both kinetic studies and sorption capacity studies.

Kinetic studies: The time-dependent studies for the removal of different anions from water were conducted using UV-visible spectroscopy. A stock solution of the anion to be captured was first prepared, followed by dilution of the stock solution to a pre-determined concentration. The absorbance for the diluted solution was recorded. Next, a fixed quantity of iCOF-2 was added to a specific volume of solution of known concentration with steady stirring. UV-visible spectrum of the supernatant liquid was recorded after diluting it to the same concentration at which the absorbance of other solutions were recorded. From the obtained data, the % removal of the anionic pollutants was calculated using equation (1)

% removal =
$$
\frac{c_0 - c_t}{c_0} \times 100\%
$$
.................(1)

Where C_0 (mM) is the initial concentration of the anionic pollutants and C_t (mM) is the pollutant concentration at time t . Subsequently, the data was fitted with the non-linear pseudosecond order equations equation (2) for kinetics

$$
Q_t = \frac{K_2 Q_e^2 t}{1 + K Q_e t} \tag{2}
$$

where Q_t (mg/g) and Q_e (mg/g) are the amounts of sorbate captured by iCOF-2 (sorbent) at different time intervals (*t*) and at equilibrium respectively. Herein, *t* represents the time in minutes, K_2 (g mg⁻¹ min⁻¹) are the rate constants for pseudo first-order and pseudo-second order reactions respectively.

*K***^d calculation formula**

$$
K_d = \left(\frac{c_o - c_f}{c_f}\right) \times \frac{v}{M} \dots \tag{3}
$$

Using the equation 3, the values of all the distribution coefficients were calculated. Here, C_0 (mM) and C_f (mM) indicate the initial and final concentrations, respectively, whereas K_d is the distribution coefficient. Further, M represents the mass of the sorbent (g), and V denotes the volume of the solution (mL).

Adsorption isotherm experiment: In this experiment, 5 mg of the adsorbent was added to 5 mL of stock solution of a given ion with different concentrations. The mixture was stirred at a constant speed of 550 rpm at room temperature for 12 hours. Subsequently, the adsorbent was filtered off with syringe filter $(0.22 \mu m)$, and the concentration of remaining (uncaptured) ions in the solution were measured by recording a UV−vis spectrum. The results obtained from these experiments were fitted with following equation (4) and (5) respectively,

Langmuir Model,

$$
Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad \dots \quad \dots \quad \dots \quad (4)
$$

Where, C_e (mg L^{-1}) and Q_e (mg g^{-1}) are the concentration of analyte at equilibrium and amount of analyte adsorbed at equilibrium respectively. Q_m (mg g^{-1}) is the maximum amount of analyte per mass of adsorbent to form a complete monolayer. K_L (mg L^{-1}) is a constant related to the affinity of the binding sites.

Freundlich Model,

$$
Q_e = K_F C_e^{1/n} \dots \tag{5}
$$

Where, K_f and $1/n$ are the Freundlich model constant, indicating capacity and intensity of adsorption respectively.

Iodine sorption experiments in vapor phase:

In this experiment, 20 mg of iCOF-2 was taken in a sealed chamber and exposed to iodine vapor for over 48 hours at 75 ℃ and ambient pressure. In this experiment, initially the polymer sample was activated and placed in a small open vial (5 ml capacity). Next, this small vial was placed inside another larger vial (15 ml capacity) to avoid the direct contamination. Then, the larger vial (15 ml capacity) was further kept inside a glass chamber with iodine granules present at the bottom. Subsequently, glass chamber was sealed and kept in an oven at 75 °C. Periodically, the weight of the smallest vial (5 ml capacity and containing iCOF-2) was recorded. A gradual but significant colour change was observed in iCOF-2 with the onset of iodine adsorption till the experiment ended. The iodine uptake capacities were calculated using the equation (6).

$$
\alpha = \frac{m_2 \cdot m_1}{m_1} \dots \tag{6}
$$

where α is the iodine uptake capacity in g/g and m₁, m₂ are the weight of the vial containing iCOF-2 before and after the start of the iodine vapor capture experiment.

Real-time experiments: 0.25 mM stock solutions of the pollutants were prepared using water collected for tap, tannery, pond, lake, river and sea. To 5 ml of these solutions, 10 mg of iCOF-2 was added and the mixture was stirred for 3 hours. The adsorbent (iCOF-2) was then filtered out and the filtrate was analysed using UV-vis spectroscopy. The uptake capacities were calculated from the values of the initial and final absorbance of the filtrate.

Selectivity studies: 5 mg of iCOF-2 was introduced to a binary solution consisting of 5 mL of 0.1 mM of the target anionic pollutant (MnO₄⁻, ReO₄⁻, CrO₄²⁻, Cr₂O₇²⁻, MnO₄⁻, I₃⁻, diclofenac sodium) and 5 ml of 0.1 mM solutions containing various interfering ions $(Cl^-, Br^-$, NO₃^{$-$} and SO₄^{2 $-$}). The mixture was then filtered and the filtrate was analysed using UV-vis spectroscopy. For 1:20 ratio of interfering ions, the analyte concentration changes respectively.

Regeneration studies: Post anion capture experiments, iCOF-2 loaded with pollutants were regenerated by treating such samples with a dilute solution of NaOH, dilute HCl or 1:1 mixture of MeOH and saturated brine in sequence.

Fig. S17a: Time dependent UV-vis spectra of MnO₄

Fig. S17b: Concentration change of MnO₄⁻ with time.

Fig. S17c: Pseudo second order kinetic rate model fitting for MnO₄⁻ capture.

Fig. S17d: MnO₄⁻ removal with 1:1 ratio of other interfering anions

Fig. S17e: Isotherm fitting for MnO₄⁻ capture

Fig. S18a: Time dependent UV-vis spectra of ReO₄⁻ capture experiment

Fig. S18b: Decrease in the concentration of ReO_4 ⁻ with time

Fig. S18c: Pseudo second order kinetic rate model fitting of ReO₄⁻ capture data.

Fig. S19a: Time dependent UV-vis spectra of I_3 ⁻ capture from its aqueous solution

Fig. S19b: Change in the concentration of I₃⁻with time

Fig. S19c: Pseudo second order kinetic rate model fitting of I_3 ⁻⁻ capture data

Fig. S19d: Isotherm fitting for I_3 ^{$-$} capture

Fig. S19e: Gravimetric iodine capture by iCOF-2

Fig. S20a: Time dependent capture of CrO₄^{2—} using UV-vis spectroscopy

Fig. S20b: Time dependent percentage removal of CrO₄^{2–}

Fig. S20c: Change in CrO₄^{2—}concentration with time

Fig. S20d: Isotherm fitting for CrO_4^2 capture

Fig. S21a: Time dependent UV-vis spectra of $Cr_2O_7^2$ capture from its aqueous solution

Fig. S21b: Change in the concentration of $Cr_2O_7^2$ with time

Fig. S22a: % removal vs time of DCF

Fig. S22b: Decrease in the concentration of DCF with time

Fig. S22c: Pseudo second order kinetic rate model fitting of DCF⁻ capture

Fig. S22d: DCF— removal in presence of other interfering anions

Fig. S23: (a) Column based capture of $MnO₄⁻$ (b) UV-vis spectra of column eluted solution $MnO₄⁻$ (c) Column based capture of I₃⁻ (d) UV-vis spectra of column eluted solution I₃⁻

Fig. S24: (a) Packing of i-COF-2 (b) Bulk purification of MnO₄⁻ contaminated water with a MnO₄⁻ as a model pollutant (c) UV-vis spectra of eluted solution I_3 ⁻ (d) UV-vis spectra solution of MnO₄

Fig. S25: Removal experiments after acid/base treatment of pristine iCOF-2

Fig. S26: Reusability of iCOF-2 for different anionic pollutants.

Fig. S27a: Post-capture FT-IR spectra of iCOF-2@MnO₄⁻ compared with pristine iCOF-2

Fig. S27b: Post-capture FT-IR spectra iCOF-2@ of I₃⁻ and pristine iCOF-2.

Fig. S27c: Post-capture FT-IR spectra of iCOF-2@DCF— and pristine iCOF-2.

Fig. S27d: Post-capture FT-IR spectra of $CrO₄²$ = @iCOF-2 and pristine iCOF-2.

Fig. S28: Post capture FE-SEM images of (a) I_3 ⁻ @iCOF-2 (b) CrO₄²⁻ @iCOF-2, (c) ReO₄⁻ @iCOF-2

Fig. S29: Raman spectrum of (a) iodine captured iCOF-2 (b) Pristine iCOF-2

Fig. S30: TGA thermogram of iCOF-2@ I₃⁻and pristine iCOF-2.

Fig. S31a EDX and elemental mapping analysis of the iCOF-2 $@$ MnO₄^{$-$}

Element	Weight	Atomic%	
	%		
C K	43.88	54.88	
NK	25.91	27.78	c
OK	17.33	16.27	
$ $ CI K	0.10	0.04	
Re M	12.78	1.03	Re MO Re Re CI CI
			2.5 3.5 0.5 1.5 3 4
Totals	100.00		Full Scale 32378 cts Cursor: 0.802 (206 cts)

Fig. S31b EDX analysis of the iCOF-2 $@$ ReO₄^{$-$}

Element	Weight%	Atomic%									
C K	39.29	58.70									
NK	18.78	24.06									
OK	11.29	12.66									
CIK	0.70	0.36									
ПL	29.93	4.23									
			NO			CI CI					
Totals	100.00		0.5 Full Scale 54232 cts Cursor: 0.000	1.5	$\overline{2}$	2.5	3	3.5	4.5	5	5.5

Fig. S31c EDX analysis of the iCOF-2@I₃

Fig. S31d EDX and elemental mapping analysis of the iCOF-2 ω CrO₄^{2–}

Section S7:

Table-S2

N.D.= Not Done

$\text{CrO}_4{}^{2^-}$

Fig. S32: Comparisons of iCOF-2 with other adsorbents

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- 2. S. Mitra, S. Kandambeth, B. P. Biswal, A. Khayum M, C. K. Choudhury, M. Mehta, G. Kaur, S. Banerjee, A. Prabhune, S. Verma, S. Roy, U. K. Kharul and R. Banerjee, *Journal of the American Chemical Society*, 2016, **138**, 2823-2828.